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Novel Trimethylsilyl-Substituted Aminobranes

by

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Reaction of $(Me_3Si)_2NBCl_2$ and $BCl_3 \cdot NEt_3$ with $(Me_3Si)_2NB(NH_2)NHSiMe_3$ in the presence of triethylamine gave $(Me_3Si)_2NB[HNB(NHSiMe_3)N(SiMe_3)_2]_2$ and $B[HNB(NHSiMe_3)N(SiMe_3)_2]_3$, respectively. Reaction of $(Me_3Si)_2NBCl_2$ with an excess of ammonia resulted in the formation of $(Me_3Si)_2NB(NH_2)_2$ and $[(Me_3Si)_2NBNH_2]_2NH$ in the ratio ~3:1. The compounds were characterized by elemental analysis, ^1H and ^{11}B NMR, infrared spectroscopy, and mass spectrometry; all exhibited prominent molecular ions. Pyrolysis of $[(Me_3Si)_2NBNH_2]_2NH$ at 200°C resulted in the formation of several borazines.

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Novel Trimethylsilyl-Substituted Aminoboranes

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The major emphasis in the approaches to BN precursors has been centered on cyclics.[1] However, as demonstrated by Beck et al., reaction of simple adducts such as $Me_2S{\cdot}BHBr_2$ with ammonia provide alternate routes to BN.[2] Trimethylsilyl-substituted aminoboranes are also of potential interest in this application in view of their processibility, versatility, and the ease of (trimethylsilyl)amino group elimination. A number of (trimethylsilyl)amino-substituted boranes have been described.[3-10] We have prepared a bis((silylamino)boryl)amine, $[(Me_3Si)_2NBNHSiMe_3]_2NH$;[11] however, the feasibility of making longer chain B–N materials of this nature needed to be established. Shaw et al.[12] approached this problem by bridging N–B(Ph)–N with $(CH_2)_n$ units. The presence of carbon on nitrogen and boron in this system provides for carbon retention on any subsequent pyrolysis. In BN precursors a very important consideration is the avoidance of carbon substituents on boron. Earlier, Jenne and Niedenzu[13] and Nöth and co-workers[14,15] described a series of noncyclic boron–nitrogen compounds containing up to four boron atoms. However, in each of the compounds, at least some of the boron atoms were either alkyl- or aryl-substituted. Our goal was to prepare B–N chains free of B–C and N–C linkages. We wish now to report novel linear borylamines containing up to four boron atoms as well as intermediates containing free NH_2 substituents. The latter offer particularly suitable monomers for linear B–N polymer synthesis and borazine-ring-linking applications.

Experimental Section

General Procedures. Operations were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or by using standard vacuum line procedures.[16] Infrared spectra were recorded: solids as double mulls (Kel-F oil No. 10 and Nujol); liquids as capillary films on a Perkin-Elmer Model 1330 infrared spectrophotometer. The mass spectra (EI) were obtained from a Du Pont Model 21-491B spectrometer. The spectrometer was attached to a Varian Aerograph Model 2700 gas chromatograph equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. Gas chromatography was performed by employing a 3 ft × $^1/_8$ in. stainless steel column packed with 3% Dexsil 300 resin on 100/200 mesh Chromosorb W-AW. NMR spectra were recorded on a Varian VXR-200 spectrometer; for ^{11}B a 64.2-MHz operating frequency was employed. Me_4Si and $BF_3{\cdot}Et_2O$ were used as external standards for ^1H and ^{11}B NMR, respectively. Boron and nitrogen were determined by wet analysis; boron by base titration, nitrogen as NH_3 by using ion chromatography.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium, and BCl_3 by vacuum line fractional condensations; $(Me_3Si)_2NH$ (Aldrich Chemical Co.) was used as received; triethylamine (Aldrich Chemical Co.) was distilled from $LiAlH_4$. $(Me_3Si)_2NB(NH_2)NHSiMe_3$,[6] $(Me_3Si)_2NBCl_2$,[5] and $BCl_3{\cdot}NEt_3$[17] were prepared by literature procedures. All solvents were rigorously dried and degassed.

$(Me_3Si)_2NB[HNB(NHSiMe_3)N(SiMe_3)_2]_2$ (1). To a stirred solution of $(Me_3Si)_2NB(NH_2)NHSiMe_3$ (14.99 g, 54.4 mmol) in triethylamine (38 mL) was added dropwise, at room temperature, $(Me_3Si)_2NBCl_2$ (6.61 g, 27.3 mmol) over a period of 30 min; a white precipitate started to form immediately. Stirring was continued for 16 h at room temperature, followed by 6.5 h at 100 °C. After cooling, triethylamine hydrochloride, 4.15 g (55.4% yield), was filtered off. The excess triethylamine, unreacted starting materials, and byproducts were removed in vacuo by heating to 213 °C. Some of the product (13% of theoretical yield based on $(Me_3Si)_2NBCl_2$ employed) was present in the distillate as determined by GC. The product accounted for 87% of the 3.82 g of distillation residue, bringing the total yield of the material to 21.5%. Crystallization from Freon-113 gave 1.57 g of $(Me_3Si)_2NB[HNB(NHSiMe_3)N(SiMe_3)_2]_2$, mp 120–120.5 °C. Anal. Calcd for $C_{24}H_{76}N_7B_3Si_8$: N, 13.62; B, 4.50. Found: N, 13.93; B, 4.54. IR (cm^{-1}, NaCl plates): 3395 (w), 3360 (w), 3300 (m), 2950 (s), 2895 (m), 1410 (s, br), 1346 (s), 1260 (s), 1247 (s), 1143 (m), 1108 (s), 996 (s), 965 (sh),

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945 (s), 910 (m), 874 (m), 830 (s, br), 758 (s), 680 (s), 650 (w), 620 (m). MS (70 eV), *m/e* (relative intensity, ion): 719 (26.8%, M), 704 (14.6%, M − Me), 615 (11.7%, M − Me − H_2NSiMe_3), 445 (22.4%, M − $HNB(NHSiMe_3)N(SiMe_3)_2$), 259 (100% $(Me_3Si)_2NBNHSiMe_3$), 187 (10%, $H_2NBN(SiMe_3)_2$), 171 (12.8%, $BN(SiMe_3)_2$). ^1H NMR (C_6D_6): δ 0.30 (s), 3.55 (br) in the ratio 21.5:1 (theory 18:1, if $NH(SiMe_3)$ and bridging NH are unresolved). ^{11}B NMR: δ 34.8 ($h/2 \sim 682$ Hz).

$B[HNB(NHSiMe_3)N(SiMe_3)_2]_3$ (2). To a stirred refluxing solution of boron trichloride triethylamine adduct (5.09 g, 23.3 mmol) and triethylamine (7.08 g, 70.0 mmol) in benzene (15 mL) was added dropwise $(Me_3Si)_2NB(NH_2)NHSiMe_3$ (19.29 g, 70.0 mmol) over 1.5 h. Heating was then continued for another 2.5 h. Filtration gave 8.69 g (90.3% yield) of triethylamine hydrochloride. Removal of solvent from the filtrate gave 20.55 g of a thick slurry; washing with Freon-113 and then methanol resulted in isolation of a solid (6.05 g, 31.1% yield). Recrystallization from Freon-113 afforded 4.29 g (22.1% yield) of $B[NHB(NHSiMe_3)N(SiMe_3)_2]_3$, mp 128–130 °C. Anal. Calcd for $C_{27}H_{87}N_9B_4Si_9$: N, 15.11; B, 5.18. Found: N, 15.58; B, 4.76. IR (cm^{-1}, NaCl plates): 3348 (m–w), 3498 (m–w), 2955 (m), 2900 (m–w), 1430 (s), 1345 (s), 1280 (s), 1265 (s), 1250 (s), 1215 (m), 1180 (sh), 1128 (s), 973 (s), 946 (s), 875 (s), 836 (s, br), 790 (w), 755 (s), 684 (s), 630 (w), 615 (w). MS (70 eV), *m/e* (relative intensity, ion): 833 (18.7%, M), 818 (4.5%, M − Me), 575 (11.2%, M − $(Me_3Si)_2NBNSiMe_3$), 560 (16.9%, M − $NBN(SiMe_3)(NHSiMe_3)$), 259 (100%, $(Me_3Si)_2NBNHSiMe_3$), 187 (10.0%, $H_2NBN(SiMe_3)_2$), 171 (12.8%, $BN(SiMe_3)_2$). ^1H NMR: δ 0.30, 0.32 (s), 2.66 (s), 3.46 (s) in the ratio 27 (δ 0.30 and 0.32 combined):0.9:1 (theory 27:1:1). ^{11}B NMR: δ 31.4 ($h/2 \sim 1364$ Hz).

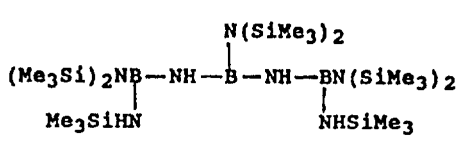
$(Me_3Si)_2NB(NH_2)_2$ (3) and $[(Me_3Si)_2NBNH_2]_2NH$ (4). To stirred liquid ammonia (~13 g held at −78 °C) was added, via an addition funnel, a solution of $(Me_3Si)_2NBCl_2$ (8.20 g, 33.9 mmol) in pentane (30 g) over a period of 1 h. Stirring at −78 °C was continued for 4 h. The mixture was then allowed to warm to room temperature overnight. The precipitated ammonium chloride (3.66 g, quantitative yield) was filtered off; the filtrate (following solvent removal in vacuo) gave 6.32 g of residue, which was separated into two portions by distillation in vacuo at 40–65 °C. The distillate, 3.88 g, bp 26–27 °C/0.001 mmHg, consisted of 80% of $(Me_3Si)_2NB(NH_2)_2$ corresponding to a 45% yield. This material was further purified by vacuum line fractionation through traps held at 0, −23, and −196 °C. The pure $(Me_3Si)_2NB(NH_2)_2$ was collected in the 0 °C trap. Anal. Calcd for $C_6H_{22}N_3BSi_2$: N, 20.67; B, 5.32. Found: N, 20.85; B, 5.31. IR (cm^{-1}, KBr plates): 3528 (m), 3435 (m), 2955 (s), 2895 (m), 1590 (s), 1445 (w), 1410 (w), 1360 (m), 1324 (s), 1285 (s), 1250 (s), 965 (s, br), 902 (m), 835 (s, br), 754 (m), 680 (m), 650 (w), 625 (w). MS (70 eV), *m/e* (relative intensity, ion): 203 (36.9%, M), 188 (100%, M − Me), 171 (86.0%, M − Me − NH_3), 130 (23.1%, $Me_3SiNSiMe$). ^1H NMR (C_6D_6): δ 0.18 (s), 1.63 (s) in the ratio 4.5:1 (theory 4.5:1). ^{11}B NMR: δ 31.9 ($h/2 = 80.2$ Hz).

$[(Me_3Si)_2NBNH_2]_2NH$ (1.89 g, 27% yield) comprised the distillation residue (95% purity based on GC). It was further purified by sublimation, mp 47–48°C. Anal. Calcd. for $C_{12}H_{41}N_5B_2Si_4$: N, 17.98; B, 5.55. Found: N, 17.25; B, 5.46. IR (cm^{-1}, KBr plates): 3525 (m), 3437 (m), 2955 (s), 2895 (m), 1594 (s), 1428 (s), 1403 (s), 1334 (s), 1300 (m), 1250 (s, br), 1153 (s), 965 (s, br), 837 (s), 755 (s), 680 (s), 650 (w), 624 (w). MS (70 eV), *m/e* (relative intensity, ion): 389 (14.1%, M), 374 (100%, M − Me), 357 (70.1%, M − Me − NH_3), 300 (11.6%, M − H_2NSiMe_3), 285 (77.1%, M − Me − H_2NSiMe_3), 269 (57.0%, M − Me − NH_3 − $NHSiMe_3$), 187 (36.3%, $H_2NBN(SiMe_3)_2$), 171 (26.0%, $BN(SiMe_3)_2$). ^1H NMR (C_6D_6): δ 0.24 (s), 2.31 (br), 2.86 (br) in the ratio 34:3.4:1 (theory 36:4:1). ^{11}B NMR: δ 33.0 ($h/2 \sim 241$ Hz).

Pyrolysis of $[(Me_3Si)_2NBNH_2]_2NH$. 4 (0.76 g, 1.95 mmol) was heated in vacuo at 200 °C for 20 h. A viscous liquid resulted. After opening to the vacuum system, the condensible volatiles (115 mg) were collected and then fractionated through −63 and −78 and into −196 °C cooled traps. $HN(SiMe_3)_2$ (93 mg, 0.59 mmol) was condensed in the −63 and −78 °C traps; NH_3 (22 mg, 1.29 mmol), in the −196 °C trap. The residue was analyzed by GC/MS; three borazines were identified: $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$,[18] $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$,[19] and $[(Me_3Si)_2NBNH]_3$,[18] in the ratio 1:13:10.

Results and Discussion

Reaction of $(Me_3Si)_2NBCl_2$ with $(Me_3Si)_2NB(NH_2)NHSiMe_3$ in a 1:2 ratio in the presence of triethylamine gave **1** in ~20% yield. The pure product was stable in air. The presence of a



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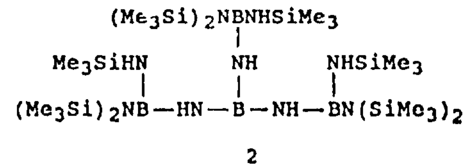
molecular ion in its mass spectrum and the fragmentation pattern fully support the above arrangement. The broad ^{11}B NMR resonance centered at 35 ppm is consistent with the data reported for related arrangements.[20] In the ^1H NMR spectrum only one NH resonance was observed. The relative ratio of the methyl protons to the nitrogen protons tends to indicate that this resonance is responsible for both the bridging NH and $NHSiMe_3$ groups. One would expect to observe two NH resonances, as in the case of the diborylamine compound.[11] The presence of $NHSiMe_3$ is shown by the strong infrared band at 1100 cm^{-1}. No pyrolysis studies were performed. However, since **1** could be analyzed by gas chromatography at 250 °C, it must be stable at least for a short period at this temperature. This is not surprising since amino(bis(trimethylsilyl)amino)boranes were found to be stable at 150–200 °C for several hours due to the shielding effect of the $(Me_3Si)_2N$ group.[10] On the other hand, at higher temperatures and in the presence of ammonia, the elimination of hexamethyldisilazane does occur.[21]

Compound **2** was obtained from the reaction of $BCl_3{\cdot}NEt_3$ with $(Me_3Si)_2NB(NH_2)NHSiMe_3$ in a 1:3 ratio in the presence of triethylamine. The analytical data obtained for **2** are in full



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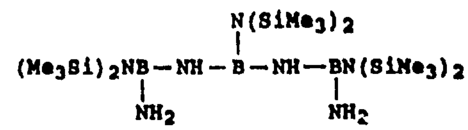
agreement with the assigned structure. In the ^1H NMR spectrum the NH protons are clearly resolved, and the observed ratios correspond closely with the theoretical values. The presence of a high-intensity molecular ion in its mass spectrum and the fragmentation pattern further confirm the arrangement. **2** was stable in air and exhibited high thermal stability, as evident by its elution from the GC column at 275 °C.

Inasmuch as the linear BN compounds can be prepared, and it is believed that the yields can be improved, the next step was to synthesize compounds containing free NH_2 groups amenable to condensation with either dihaloboranes or dihaloborazines. $(Me_3Si)_2NB(NH_2)_2$ (**3**) and $[(Me_3Si)_2NBNH_2]_2NH$ (**4**) were obtained by reacting $(Me_3Si)_2NBCl_2$ with a large excess of ammonia at −78 °C. We were unable to control conditions so as to obtain either **3** or **4** exclusively. Invariably, both materials were formed, but separation could be readily accomplished by distillation. There are a number of possible paths to **4**, namely, reaction of **3** with $(Me_3Si)_2NBCl_2$ or a mechanism involving an active intermediate such as $(Me_3Si)_2NB(NH_2)Cl$. There are no data available to postulate a specific mechanism. It is of interest that compound **5** was not observed. However, since the analyses were



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performed by GC/MS, such a material could have been retained

(18) The borazine was identified by its mass spectrum (70 eV), *m/e* (relative intensity, ion): 414 (15.1%, M), 399 (100%, M − Me), 310 (18.4%, M − Me − $H_2NHSiMe_3$).

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by the column. In view of the high, >70%, combined yield of the isolated compounds **3** and **4**, this side reaction, if it occurred, took place only to a limited extent.

The analytical data obtained for $(Me_3Si)_2NB(NH_2)_2$ and $[(Me_3Si)_2NBNH_2]_2NH$ are in agreement with the assigned structures. Both compounds exhibited in their mass spectra a high-intensity molecular ion, and the breakdown patterns were consistent with the arrangements. In each case, a prominent ion was observed corresponding to loss of a methyl group and ammonia. Ions derived by loss of ammonia were absent in the mass spectra of **1** and **2**, which is to be expected due to the absence of NH_2 groups. Neither compound exhibited an infrared absorption at ~ 1100 cm^{-1}, confirming the absence of $NHSiMe_3$ groups; both had very strong bands in the vicinity of 1600 cm^{-1}, characteristic of a NH_2 deformation mode. The ^1H NMR of **3** showed two resonances at δ 0.18 (CH_3) and 1.63 (NH_2); for **4** three resonances were observed at δ 0.18 (CH_3), 2.31 (NH_2), and 2.84 (NH), confirming the presence of the three different NH protons. The ^{11}B NMR signal was broader in **4** than in **3**, which is to be expected. The chemical shifts, 31.8 and 33.0 ppm, respectively, are consistent with the literature data.[20]

Only preliminary thermal stability studies were performed on **4**. The material was recovered essentially unchanged when exposed to 150 °C for 20 h. However, after 20 h at 200 °C, no starting material was recovered. The two borazines $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$ and $[(Me_3Si)_2NBNH]_3$ were produced in approximately equal proportions, together with a small amount of $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$.

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Registry No. **1**, 130497-70-0; **2**, 130497-71-1; **3**, 62779-47-9; **4**, 130497-72-2; $(Me_3Si)_2NB(NH_2)NHSiMe_3$, 7266-80-0; $(Me_3Si)_2NBCl_2$, 6591-26-0; $BCl_3\cdot NEt_3$, 2890-88-2; NH_3, 7664-41-7; $[(Me_3Si)_2NBNH][(Me_3Si)HNBNH]_2$, 130497-73-3; $[(Me_3Si)_2NBNH]_2[(Me_3Si)HNBNH]$, 130497-74-4; $[(Me_3Si)_2NBNH]_3$, 113665-33-1.

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